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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to Process and Apparatus for Gas Analysis

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to gas analysers and is particularly concerned with a process and apparatus for the detection and analysis of the components of gas compositions.

The present invention concerns an improvement or modification of the process and apparatus described in Patent Specification 986011 in which an element of a responsive material having piezo-electric or magneto-strictive properties is used in the detection and analysis of components in a gas stream. As described in that application, changes in the oscillation characteristics of the element, e.g. the frequency or amplitude of the oscillation, are related to changes in the weight of a substrate material deposited on the surface of the element. The substrate material is sensitive to changes in its environment, e.g. by reacting with, adsorbing, or absorbing selectively, components of the gas stream.

According to the present invention, more than two such elements of responsive material are used in the analysis of a gas stream, at least two of the elements having a substrate material thereon, each substrate material having different response characteristics in relation to the components of the gas stream, and the differences in the oscillation characteristics of different pairs of elements are compared to characterise particular components of the gas stream.

Thus, by using n elements ($n>2$), each having a substrate material thereon with different response characteristics in relation to the components of the gas stream, and by observing differences in the oscillation characteristics of all combinations of pairs of elements, $m=\frac{n}{2}(n-1)$ different results will be obtained, from which up to $\frac{m}{2}(m-1)$ deductions may be made about the nature or concentration of components of the gas stream, i.e. up to $\frac{n}{8}(n-1)(n-2)(n+1)$ deductions.

A particular useful embodiment of the invention consists in using the method and apparatus in conjunction with a gas chromatographic process for separating the components of the gas stream and presenting them sequentially to each element. Ideally, each component will be presented singly to each pair of elements. A result depending on the difference between the oscillation characteristics of each pair of elements will then be obtained for each component of the gas stream, and a deduction about each component of the gas stream can be made from any two of such results.

It is preferred to use crystals of piezo-electric material, e.g. quartz crystals, as the elements, and to compare the differences in frequency of oscillation of each pair of crystals. Independent frequency and temperature control may be provided for each crystal, so that optimum conditions for each crystal or each pair of crystals may be obtained for the detection and/or estimation of a particular

component or type of component in the gas stream.

In order that the nature of the invention may be more readily understood, the following example of one embodiment of the invention is given.

Suppose that the apparatus of the invention comprises four elements of responsive material A, B, C and D, having the following characteristics:

A is an element with no substrate material thereon, whose oscillation characteristics will not vary with the nature of the component of a gas stream presented to it;

B is a similar element to A, coated with a non-polar substrate material, whose oscillation characteristics will vary according to the boiling point of components presented to it, but will have the same response to all components of the same boiling point;

C is a similar element to A, coated with a highly polar substrate, whose oscillation characteristics will vary according to the type of component presented to it, e.g. its response to alkanes, alkenes and aromatic hydrocarbons of the same boiling point varies in the ratio of 1 to 2 to 10, respectively, i.e. unit mole % concentrations of such components will give responses in that ratio; and D is a similar element to A, coated with a slightly polar solvent whose oscillation characteristics will vary in a different way from C, e.g. its response to alkanes, alkenes and aromatic hydrocarbons varies in the ratio of 1 to 4 to 2, respectively.

On presenting a mixed hydrocarbon gas stream, whose components have been separated by passage through a chromatographic column, to the pairs A and B, A and C, and A and D in turn, the following results are obtained. Using A and B, the difference between the oscillation characteristics of the pair of elements is of magnitude x for one particular component. Then, using A and C, the difference is of magnitude 10x for the same component. Finally, using A and D, the difference is of magnitude 2x for the same component. By comparing the difference when using A and B with the difference using A and C, it is deduced that the component is predominantly aromatic. By comparing the difference when using A and B with the difference using A and D, it is confirmed that the component is aromatic and the presence of any alkene in the component is excluded. This latter deduction is all important, for in gas chromatography it is rarely possible to exclude the possibility of two components eluting from the column at the same time and therefore it is necessary to investigate this possibility.

The difference between the oscillation characteristics of a pair of elements is conveniently presented as a "chromatogram" in which the peaks recorded correspond to each component as it is presented to the pair of elements. The relative response ratio of the sizes of the peaks corresponding to the same component in the "chromatograms" obtained for different pairs of elements is then used as the comparison between these differences.

In practice, of course, a "chromatogram" of a large number of components is obtained using each pair of elements. If necessary, a reference compound can be included in the mixture to be analysed in order to facilitate calculation of relative response ratios.

From the foregoing, it will be seen that it is not necessary to have as many pairs of elements as there are component types to be identified, but nevertheless, it is obviously an advantage to produce a simultaneous equation containing as many different relative response ratios as possible in order to make identification more certain. The results from this sort of equation could readily be dealt with by computer techniques. In practice, other parameters such as component boiling point, and mass of solvent deposited on each crystal, have to be taken into account also, but this may be included in the calculation procedures.

In a preferred embodiment, outputs of a pair of elements with different selectivity characteristics are opposed and only a differential output is used. For the analysis of mixtures containing only two component types, this technique is ideal. The response of one element to a component type is attenuated or amplified until it exactly opposes the output from the other element of the pair due to the same component. The pair will now only "see" components of different types to the one "removed" and the "remaining" component can be analysed in the presence of unknown amounts of the "removed" component.

Another embodiment of the invention will now be described, by way of example, with reference to the drawing accompanying the provisional specification in which six separate elements of responsive material, with their associated oscillator circuits and temperature control devices, are used and means are provided for obtaining a signal proportional to the "beat" frequency between any two of the elements, i.e. 15 different output signals are obtainable, from which up to 105 different deductions about components of a gas stream can theoretically be made.

As the components may be supplied sequentially to each pair of elements as they elute from a chromatographic column, any number of components can be subjected to analysis. The larger the number of different pairs of elements, the more positive a qualitative identification of each component may be made. When completely selective elements can be provided, individual components can be analysed exactly, but this will be rare in practice.

If desired, one or more pairs of elements may be used to determine properties of the

gas stream other than its constituent components, e.g. its pressure, temperature or density.

Referring to the drawing, a sample of gas to be analysed is injected into a carrier gas which is passed through a chromatographic separating column 1. The effluent from the column is passed through 6 different detectors 2a, 2b, 2c, 2d, 2e and 2f, in each of which the gas is passed over a piezo-electric crystal having a different substrate material thereon. One of the detectors may contain a crystal with no substrate material on it. Alternatively the gas stream may be passed through the selected pair of detectors (referred to below) only. Each detector has its own temperature control system, e.g. an element heated electrically and controlled by a rheostat or other device of variable resistance. The crystal in each detector is connected by electrodes to an oscillator 3a, 3b, 3c, 3d, 3e or 3f, respectively, so that response of each crystal to a component in the gas stream causes a change in the frequency of the corresponding oscillator. The output of any pair of oscillators may be selected by switches 4 and 5 and passed to a mixer circuit 6, the output of which is proportional to the difference between the frequencies of the selected pair of oscillators and is presented to a recorder 7, which may incorporate a visual indicator such as a meter or a recording device such as a pen recorder. The trace of such a pen recorder will then give the "chromatogram" of the components of the gas stream as they pass through the particular pair of detectors, and the magnitude of the response of the recorder to each component of the gas stream will depend on the difference in the responses of that pair of detectors to that component. The whole process may then be repeated, selecting different pairs of detectors, and different "chromatograms" will be obtained. By comparing two or more "chromatograms", deductions and calculations may then be made about each component of the gas stream, e.g. by measuring the ratio of the areas under corresponding peaks to give relative response ratios.

WHAT WE CLAIM IS:—

1. An apparatus for the detection and analysis of the components of a gas stream, which comprises more than two elements of responsive material having piezoelectric or magnetostrictive properties, at least two of which elements have a substrate material coated thereon which interacts with the substance to be detected, each substrate material having different response characteristics in relation to the components of the gas stream, means for passing the gas stream over each of the said elements, means for oscillating each of the elements, and means for determining differences in the oscillation characteristics of different pairs of elements.

2. An apparatus as claimed in claim 1, in which chromatographic means are provided for separating components of the gas stream before it is passed over the elements, whereby the said components are presented sequentially to each element.

3. An apparatus as claimed in either of claims 1 and 2 in which the elements are made of quartz.

4. An apparatus for the detection and analysis of the components of a gas stream substantially as hereinbefore described with particular reference to the drawing accompanying the provisional specification.

5. A method for the detection and analysis of the components of a gas stream, in which the gas stream is passed over the elements of responsive material of the apparatus as claimed in claim 1, the differences in the oscillation characteristics of different pairs of elements are determined, and such differences are compared to characterise particular components of the gas stream.

6. A method as claimed in claim 5, in which the gas stream is subjected to a chromatographic process to separate components of the gas stream before it is passed over the elements, whereby the said components are presented sequentially to each element.

7. A method as claimed in either of claims 5 and 6 in which the gas stream contains only two component types and the outputs of a pair of responsive elements with different selectivity characteristics are opposed and only a differential output is used.

8. A method for the detection and analysis of the components of a gas stream substantially as hereinbefore described and in particular as described with reference to the drawing accompanying the provisional specification.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*